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(54) UNSATURATED EPOXIDES AS COUPLING AGENTS FOR CARBON FIBRES AND UNSATURATED MATRIX RESINS

(71) We, HERCULES INCORPORATED, a Corporation organised under the laws of the State of Delaware, United States of America, of 910 Market Street, City of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improving adhesion between carbon fibers and unsaturated matrix resins. More particularly it relates to the use of an unsaturated epoxide compound as a bi-functional coupling agent to improve adhesion between carbon fibers and unsaturated matrix resins.

The term "carbon fibers" is used in this application in its generic sense and includes all fibers which consist essentially of carbon ranging from graphite fibers to amorphous carbon fibers. Graphite fibers are defined herein as fibers which consist essentially of carbon and have a predominant X-ray diffraction pattern characteristic of graphite. Amorphous carbon fibers on the other hand are defined as fibers which consist essentially of carbon and which have an essentially amorphous X-ray diffraction pattern. Carbon fibers can be prepared by known processes from polymeric fibrous material, such as polyacrylonitrile, polyvinyl alcohol, pitch, natural and regenerated cellulose, which processes include the steps of carbonising or graphitizing the fiber.

A major use of carbon fibers is in the preparation of composites using a variety of different matrix resins. However, it has been observed that adhesion between carbon fibers and unsaturated matrix resins is generally lower than that desired.

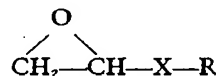
Now, in accordance with this invention, it has been discovered that composites having improved adhesion between carbon fibers and unsaturated matrix resins can be obtained by

use of certain unsaturated epoxide bifunctional coupling agents.

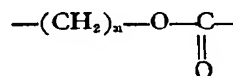
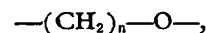
Accordingly, this invention comprises a moulding composition or a composite structure composed of (a) carbon fibers, (b) an unsaturated matrix resin and (c) an unsaturated epoxide bifunctional coupling agent.

Another aspect of this invention comprises a process of improving the adhesion of carbon fibers and an unsaturated matrix resin by incorporating into said matrix resin an unsaturated epoxide bifunctional coupling agent. The mixture of matrix resin and coupling agent may be heated to cure the mixture after the addition of the carbon fibres.

Another aspect of this invention provides a process for modifying the surface of carbon fibres to improve their ability to adhere to an unsaturated matrix resin comprising pretreating the carbon fibres of necessary to render them adhesionable or reactive with epoxide groups, and then treating the surface of the carbon fibres with an unsaturated epoxide bi-functional coupling agent having the general structural formula:



wherein X is



where $n = 1 - 10$;

or a divalent alkyl, aryl, aralkyl or alkaryl radical containing up to 20 carbon atoms, and R is an ethylenically unsaturated radical. Another aspect of this invention comprises carbon fibers having the surface thereof modified with an unsaturated epoxide. Where the

coupling agent is to be used with carbon fiber and ethylenically unsaturated matrix resin, R is (a) an ethylenically unsaturated C_1-C_4 aliphatic radical, (b) an aryl radical containing an ethylenically unsaturated C_1-C_4 aliphatic substituent, (c) the alpha-terpinyl radical, (d) the gamma-terpinyl radical or (e) the abietyl radical. When the coupling agent is to be used with carbon fiber and a poly(arylacetylene)-based matrix system, R is any ethylenically unsaturated radical.

Illustrative examples of unsaturated epoxides suitable for use with any unsaturated matrix resin are unsaturated glycidyl ethers and esters, including vinyl glycidyl ether, allyl glycidyl ether, ortho-allyl phenyl glycidyl ether, 5,6-epoxy-n-hexyl allyl ether, 2',3'-epoxypropyl 3-butenyl ether, 9,10-epoxy-n-decyl vinyl ether, glycidyl alpha-terpinyl ether, glycidyl gamma-terpinyl ether, 1-allyl-4-(epoxyethyl)benzene, 1-vinyl-4-(epoxyethyl)benzene, 1,2-epoxy-3-butene, 1,2-epoxy-5-hexene, 1,2-epoxy-9-decene, 1,2-epoxy-17-octadecene, glycidyl acrylate, glycidyl methacrylate, glycidyl crotonate, 5,6-epoxy-n-hexyl methacrylate, 9,10-epoxy-decyl crotonate and glycidyl abietate.

Illustrative examples of unsaturated epoxides which in addition to the above are suitable for use as a coupling agent between carbon fibres and poly(arylacetylene) matrix systems are vinyl cyclohexyl glycidyl ether, glycidyl-4-hexenoate, glycidyl-4-heptenoate, glycidyl 5-methyl-4-heptanoate, glycidyl sorbate, glycidyl linoleate, glycidyl oleate, glycidyl 3-butenate, glycidyl 3-pentenoate, glycidyl 4-methyl-3-pentenoate, the glycidyl ester of 2-cyclohexene carboxylic acid and the glycidyl ester of 4-methyl-3-cyclohexene carboxylic acid.

In a preferred process the poly(arylacetylene) matrix resin system comprises (1) a prepolymer of at least one polyacetylenically substituted aromatic compound, said prepolymer having a number average molecular weight from 900 to 12,000, a ratio of aromatic protons to olefinic protons greater than 2.4 and containing from 5 to 20 per cent acetylenic groups by weight of the prepolymer, with (2) from 2 to 200 per cent by weight of the prepolymer of at least one aromatic organic compound containing at least two six-membered aromatic rings such as anthracene, said rings being condensed with each other or coupled with each other directly or through a methylene, dimethylmethylene, ethylene or vinylene group, said compound or mixtures thereof containing no crystalline organic phase at 220°C., having a viscosity of less than 20 centipoises at 220°C and containing no more than 5 per cent of material volatile at 240°C. The prepolymer may for instance be a polymer of diethynylbenzene, particularly a copolymer of diethynylbenzene and diphenylbutadiene or phenylacetylene.

The following Examples serve to illustrate the various aspects of this invention. In these Examples parts and percentages are by weight unless otherwise specified.

Example 1.

Carbon fibre which has been electrolytically surface treated is passed through a 2 per cent by volume solution of allyl glycidyl ether (AGE) in ethylene dichloride. This coats the fibre with AGE solution. The coated fibre is then heated to 200°C for 2 minutes to evaporate the ethylene dichloride solvent. The amount of allyl glycidyl ether deposited on the fibre is 0.8 per cent by weight, based on the weight of fibre. The fibre is then heated at 125°C for 1 hour to react the allyl glycidyl ether with the carbon fibre surface.

Example 2.

The procedure of Example 1 was repeated using glycidyl acrylate in place of allyl glycidyl ether to modify the surface of carbon fibre.

Examples 3—10.

Carbon fibres, modified in accordance with Examples 1 and 2, unmodified, and optionally sized as indicated in Table 1 are used to prepare composites. In these Examples the matrix resin employed is a styrene modified unsaturated polyester prepared from isophthalic acid, maleic anhydride and propylene glycol in a ratio of ratio of 1:1:2 and modified with 42% by weight styrene. The curing agent or hardener employed in this resin system is 1% by weight, based on the weight of the resin, of t-butyl-perbenzoate.

In Examples 5 and 6 the carbon fiber is coated with 1.3% by weight, based on the weight of the fiber, of the styrene-modified unsaturated polyester resin as a protective size before formation of the composite.

In Examples 8 and 9 allyl glycidyl ether is dissolved in the matrix resin system.

The composite specimens are made in the form of an NOL ring containing about 60% by volume of treated graphite fiber. In preparation of the composite, the graphite fiber is passed through the unsaturated polyester matrix resin system, through a tensioning device and onto a rotating mold. The whole system is enclosed in a vacuum chamber to provide a low void composite specimen. The mold is removed from the NOL device and placed in a curing oven for one hour to harden the resin. The acronym "NOL" refers to the U.S. Naval Ordnance Laboratory, at Silver Springs, Maryland, U.S.A. A discussion of NOL ring specimens and their manufacture may be found in *Plastics Technology*, November 1958, pp.1017—24, and *Proceedings of 21st Annual Technical Conference SPI Reinforced Plastics Division*, Section 8-D, February 1966.

Composite samples prepared as described

are tested for short beam shear strength in accordance with ASTM-2344. The results of short beam shear strength tests are shown in Table I.

5 Examples 11—14.

Carbon fibers, unmodified or modified with allyl glycidyl ether in accordance with Example 1 are used to prepare composites using a poly-(arylacetylene) matrix resin system. The resin system contains a prepolymer and a fluidizer and is prepared as follows.

10 A polymerization vessel is charged with a mixture of 630 parts of meta-diethynylbenzene and 70 parts of para-diethynylbenzene dissolved in 3077 parts of anhydrous benzene. The solution is sparged with nitrogen and heated to reflux temperature. Then a catalyst mixture is added to the refluxing solution in four approximately equal increments prepared by mixing 4.4 parts of nickel acetylacetonate and 8.8 parts of triphenylphosphine in 50 parts of anhydrous benzene. After addition of the initial increment, the others are separately added one, two and three hours later. The solution is held at reflux temperature for a total of six and one-quarter hours, at which time the monomer conversion is 85.5%. The

prepolymer then is precipitated by adding the solution to seven times its volume of petroleum ether. The yellow powder, which is separated by filtration amounts to 406 parts. The prepolymer contains 11.8% acetylene groups.

A molding composition is prepared by dissolving in acetone the prepolymer and, as a fluidizer, a high boiling aromatic coal tar pitch. The amount of coal tar pitch used is 20%, by weight, based on the weight of the prepolymer. The acetone solvent is then removed in a rotary evacuator. The compositions are dried under vacuum for 16 hours at room temperature, followed by one hour at 60° C. The resulting molding composition is used with unmodified and allyl glycidyl modified carbon fibers to prepare composite NOL rings as described in Examples 3—10. The resulting composite NOL rings are tested for short beam shear strength. The results are shown in Table I.

The results in Table I show the improved adhesion, as measured by short beam shear strength, between carbon fibers and unsaturated matrix resins when allyl glycidyl ether or glycidyl acrylate is used as a coupling agent.

TABLE I

Ex.	Carbon Fiber	Matrix Resin System	Composite Short Beam Shear Strength (psi)
3	Unmodified	Unsaturated polyester	7,700
4	AGE modified (Ex. 1)	„	11,870
5	Sized with unsaturated polyester	„	9,100
6	Sized with unsaturated polyester + AGE	„	11,200
7	AGE modified (Ex. 1) then sized with unsaturated polyester	„	10,600
8	Unmodified	Unsaturated polyester containing 1% AGE	10,300
9	Unmodified	Unsaturated polyester containing 5% AGE	10,600
10'	Glycidyl Acrylate Modified (Ex. 2)	Unsaturated polyester	10,715
11	Unmodified	Poly(arylacetylene) + fluidizer	6,070
12	AGE modifier (Ex. 1)	„	9,400
13	Unmodified	„	6,620
14	AGE modified (Ex. 1)	„	10,570

Carbon fibers employed in accordance with this invention must have a surface adhesionable or reactive with epoxide groups. To improve the adhesion between the carbon fiber surface and epoxide groups the carbon fiber surface can be pretreated, for example, by electrolytic treatment or by oxidation.

One method of employing coupling agents in accordance with this invention is to apply the coupling agent onto the fiber prior to forming the composite. The coupling agent is generally applied to the fiber in the form of a solution in a suitable solvent followed by removal of the solvent by air drying or by heating to effect evaporation. Examples of suitable solvents are benzene, polar solvents, such as halogenated hydrocarbons, for example, methylene chloride and ethylene dichloride, diacetone alcohol, ketones and esters. However, if the coupling agent is liquid, no solvent is necessary and the coupling agent can be applied directly onto the fiber.

The concentration of the coupling agent in the solvent, if one is used, is usually in the range of 0.5 to 5.0%, preferably 1.0 to 3.0% by weight, based on the total weight of the solution. The solution can be applied to the fiber by known methods, for example, by drawing the fiber through a bath containing the solution or by spraying the solution onto the fiber.

The amount of coupling agent applied to the fiber surface is from 0.05 to 10.0% by weight, based on the weight of the fiber, and is preferably from 0.5 to 3.0%.

To protect the surface modified carbon fiber of this invention from abrasion during subsequent handling, a size can be applied to the carbon fiber. The size can be applied from the same solution as the coupling agent or it can be applied after the carbon fiber has been modified with the coupling agent. The size selected for application to the carbon fiber will be one compatible with the unsaturated matrix resin to be used in preparing the final composite.

An alternate method of employing the coupling agent in accordance with this invention is to incorporate the unsaturated epoxide into the unsaturated matrix resin system to be used in preparing the composite. The coupling agent is used in an amount from 1 to 5% by weight, based on the weight of the matrix resin system.

Composites of carbon fibers and unsaturated matrix resins can be prepared by any of the known methods. For example, carbon fibers can be used to prepare filament wound composites. In another common method, the composite is prepared by incorporating chopped carbon fibers into the matrix resin and then forming the composite, for example, by press molding.

Any type of unsaturated polymer can be used as the matrix resin to prepare compo-

sites in accordance with this invention. Illustrative examples of these polymers are polybutadiene - 1,2; polybutadiene - 1,4; styrene-butadiene copolymers; butyl rubber (polyisobutylene-isoprene copolymers); natural rubber; polyester resins such as, for example, maleate containing polyesters and polyacrylate esters; butadiene-acrylonitrile copolymers; ethylene-propylene-dicyclopentadiene terpolymers; polychloroprene; polyisoprene; alkyd resins, such as for example, tall oil alkyd resins; and polyether copolymers and terpolymers containing at least one unsaturated epoxide constituent such as; for example, propylene oxide-allyl glycidyl ether copolymers and ethylene oxide-epichlorohydrin-allyl glycidyl ether terpolymers. Poly(arylacetylene)-fluidizer thermosetting molding compositions are also suitable matrix resin systems.

Illustrative examples of unsaturated polyesters are prepared from polyhydric alcohols and unsaturated polycarboxylic acids or their anhydrides, optionally along with saturated polycarboxylic acids by methods well known in the art. These polyesters generally have a molecular weight of 500 to 3000 and an acid number and a hydroxyl number in each case of 20 to 50.

Examples of polyhydric alcohols which can be employed in preparation of unsaturated polyesters are ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, butene-1,4-diol, dimethylpropane-1,3-diol, diethyleneglycol, dipropyleneglycol, dimethylolcyclohexane and bis-(hydroxyethyl)- or bis-(hydroxypropyl)diphenylolmethane or propane. Examples of unsaturated carboxylic acids are maleic acid, fumaric acid, itaconic acid and the like. Examples of saturated (i.e., free from aliphatic multiple bonds) polycarboxylic acids are phthalic acid, isophthalic acid, terephthalic acid, succinic acid, adipic acid, sebacic acid, azelaic acid, suberic acid and cyclohexanedicarboxylic acid and their existing anhydrides. The saturated dicarboxylic acids are generally used in a proportion of 0 to 90; preferably 0 to 70 mol percent.

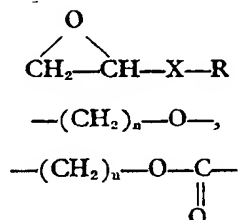
The unsaturated polyesters are usually employed along with copolymerizable monomers when used as a matrix resin for preparing composites. The ratio of monomer to polyester is usually in the range of 30:70 to 90:10. Examples of suitable monomers include styrene, vinyltoluene, alkylstyrenes, such as α -methyl- or tert-butylstyrene, diallyl phthalate, divinylbenzene, and esters of methacrylic or acrylic acid.

Examples of poly(arylacetylene) matrix resin systems are the thermosetting molding compositions described in U.S. Patent 3,882,073, May 6, 1975, to L. C. Cessna.

WHAT WE CLAIM IS:—

1. A process for modifying the surface of

carbon fibres to improve their ability to adhere to an unsaturated matrix resin, comprising pre-treating the carbon fibres if necessary to render them adhesionable or reactive with epoxide groups, and treating the surface of the carbon fibres with an unsaturated epoxide bifunctional coupling agent having the general structural formula:



where $n = 1-10$;

or a divalent alkyl, aryl, aralkyl or alkaryl radical containing up to 20 carbon atoms, and R is an ethylenically unsaturated radical.

2. A process according to Claim 1, wherein R is

(a) an ethylenically unsaturated C_1-C_4 aliphatic radical,

(b) an aryl radical containing an ethylenically unsaturated C_1-C_4 aliphatic substituent,

(c) an alpha-terpinyl radical,

(d) a gamma-terpinyl radical, or

(e) an abietyl radical.

3. A process according to Claim 2, wherein the coupling agent is incorporated into an ethylenically unsaturated matrix resin before being placed in contact with the surface of the carbon fibres.

4. A process according to Claim 3, wherein the mixture of matrix resin and coupling agent is heated to cure the mixture after the addition of the carbon fibres.

5. A process according to any of Claims 1 to 4, wherein said bifunctional coupling agent is an unsaturated glycidyl ether.

6. A process according to Claim 5, wherein said bifunctional coupling agent is allyl glycidyl ether.

7. A process according to any of Claims 1 to 4, wherein said bifunctional coupling agent is an unsaturated glycidyl ester.

8. A process according to Claim 7, wherein said bifunctional coupling agent is glycidyl acrylate.

9. A process according to any of Claims 3 to 8, wherein said unsaturated matrix resin is an unsaturated polyester resin.

10. A process according to Claim 9, wherein said unsaturated polyester resin is a styrene modified unsaturated polyester derived from isophthalic acid, maleic anhydride and propylene glycol.

11. A process according to Claim 9, wherein

said unsaturated matrix resin is a poly(arylacetylene) resin system.

12. A process according to Claim 11, wherein said poly(arylacetylene) matrix resin system comprises (1) a prepolymer of at least one polyacetylenically substituted aromatic compound, said prepolymer having a number average molecular weight from 900 to 12,000, a ratio of aromatic protons to olefinic protons greater than 2.4 and containing from 5 to 20 per cent acetylenic groups by weight of the prepolymer, with (2) from 2 to 200 per cent by weight of the prepolymer of at least one aromatic organic compound containing at least two six-membered aromatic rings, said rings being condensed with each other or coupled with each other directly or through a methylene, dimethylmethylene, ethylene or vinylene group, said compound or mixtures thereof containing no crystalline organic phase at 220°C ., having a viscosity of less than 20 centipoises at 220°C and containing no more than 5 per cent of material volatile at 240°C .

13. A process according to Claim 12, wherein the prepolymer comprises a polymer of a diethynylbenzene.

14. A process according to Claim 13, wherein the polymer of a diethynylbenzene is a copolymer of a diethynylbenzene and diphenylbutadiene.

15. A process according to Claim 13, wherein the polymer of a diethynylbenzene is a copolymer of a diethynylbenzene and phenylacetylene.

16. A process according to any of Claims 12 to 15, wherein the aromatic organic compound is anthracene.

17. A process according to any of Claims 12 to 15, wherein the aromatic organic compound is the complex mixture of high boiling aromatic compounds present in high boiling fractions of coal tar pitch.

18. A process according to Claim 1, substantially as described in the foregoing Examples.

19. Carbon fibres having the surface thereof modified by a process according to any preceding Claim.

20. A process of improving the adhesion between carbon fibres and an unsaturated matrix resin in a carbon fibre reinforced composite structure, comprising modifying the surface of said carbon fibres by the process of Claim 1, admixing the surface modified carbon fibres and the unsaturated matrix resin, and curing the resulting mixture, the unsaturated matrix resin being a poly(arylacetylene) resin system.

21. A process of improving the adhesion between carbon fibres and an ethylenically unsaturated matrix resin in a carbon fibre reinforced composite structure, comprising

- modifying the surface of said carbon fibres by the process of Claim 2, admixing the surface modified carbon fibres and the ethylenically unsaturated resin, and curing the resulting mixture.
22. A process as claimed in Claim 20 or 21, wherein the coupling agent is as defined in any of Claims 5 to 8.
23. A process of improving the adhesion between carbon fibres and an unsaturated matrix resin in a carbon fibre reinforced composite structure comprising incorporating into a mixture of said matrix and carbon fibres a coupling agent as defined in any of Claims 1 to 5 and 8, and curing the resulting mixture, the unsaturated matrix resin being a poly-(arylacetylene) resin system.
24. A process of improving the adhesion between carbon fibres and an ethylenically unsaturated matrix resin in a carbon fibre reinforced composite structure, comprising incorporating into a mixture of said matrix and carbon fibres a coupling agent as defined in any of Claims 2 and 5 to 8, and curing the resulting mixture.
25. A composite structure which is a cured mixture produced by the process of any of Claims 20 to 24.
26. A mouldable composition comprising carbon fibres in a poly(arylacetylene) resin matrix, and incorporating a coupling agent in the composition, the coupling agent being as defined in any of Claims 1 and 5 to 8.
27. A mouldable composition comprising carbon fibres in an ethylenically unsaturated polymeric resin matrix, and incorporating a coupling agent in the composition, the coupling agent being as defined in any of Claims 2 and 5 to 8.
28. A mouldable composition according to Claim 26, wherein the resin matrix is as defined in any of Claims 9 to 17.

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